Amendments to the Claims

This listing of claims will replace all prior versions, and listings, of claims in the application:

Complete Listing of Claims:

1. (Original) A method of making a functionalised polymer of Formula (1) or Formula (2).

$$R1 - \left[Q - \right]_{q} - R'$$
(1)

$$\left[R1 - \left[Q\right]_{q}\right]_{p} R'$$
(2)

comprising the steps of:

reacting a thiocarbonyl thio compound of Formula (3) or Formula (4);

$$z = \begin{bmatrix} S \\ -S - R^{1} \end{bmatrix}_{m}$$
 (3),

$$\left[z^{-}\right]_{p}^{S}R^{b}$$
(4)

an olefinically unsaturated monomer (Q), and a first source of free radical to form a Polymer of Formula (6) or Formula (7);

$$z = \begin{bmatrix} S \\ -Q \end{bmatrix}_{q} = R' \end{bmatrix}_{m}$$
(6)

$$\left[z - S - \left[Q - \frac{1}{q}\right]_{p} R'\right]$$
(7)

and subsequently contacting the polymer of Formula (6) or Formula (7) with a second source of free radicals, the second source of free radicals comprising a radically transferable functional moiety R1, to form a polymer of Formula (1) or Formula (2) and a compound of Formula (3) or Formula (4);

wherein:

R1 is moiety comprising a functional group;

R' is selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups;

Z is selected from (i) a solid support, (ii) Z comprises a linker attached to a solid support, and (iii) Z is a group selected from a straight or branched chain, substituted or non substituted C_1 to C_{20} alkyl (especially a C_1 to C_4 alkyl such as methyl or ethyl); optionally substituted aryl, e.g. phenyl, substituted phenyl; phenyl covalently bonded to a polymer; optionally substituted

heterocyclyl, substituted or non-substituted C_1 to C_{20} (especially C_1 alkoxy, optionally substituted alkyl thio, thioalkoxyl (optionally substituted with a polymer); substituted or nonsubstituted benzyl (optionally substituted with a solid support), optionally substituted aryl oxycarbonyl (-COOR''), carboxy (-COOH), optionally substituted ocyloxy (-O₂CR"), optionally substituted acyloxy (-CO₂CR"), optionally substituted carbomyl (-CONR"₂), cyano (-CN), dialkyl- or diaryl phosphonato (-P(=OR"Z), dialkyl- or diaryl-phosphinato [-P(=0)R"Z] or SCH₂CH₂ CO₂T (where T is a solid support or a polymer); the linker may optionally comprise a straight or branched chain, substituted or non substituted C_1 to C_{20} alkyl (especially a C_1 to C_4 alkyl such as methyl or ethyl); phenyl, substituted phenyl; phenyl covalently banded to a polymer; substituted or non-substituted C_1 to C_{20} (especially C_1 to C_4) alkoxy, thioalkoxyl (optionally substituted with a polymer); substituted or non-substituted benzyl;

most preferably Z is a solid support or a linker attached to a solid support;

R" is selected from the group consisting of optionally substituted C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxyl, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxycarbonyl, isocyanato, cyano, silyl. halo, and dialkylamino;

Q is at least one olefinically unsaturated monomer, optionally two or more different olefinically unsaturated monomers;

q = an integer of at least 2;

p = an integer of at least 1;

m = an integer of at least 1.

2. (Original) A method of making a functionalised polymer according to Claim 1, wherein the olefinically unsaturated monomer comprises vinyl monomers of Formula (5):

$$\stackrel{\mathsf{X}}{=}_{\mathsf{Y}}$$

wherein X is selected from the group consisting of: hydrogen, halogen and substituted or unsubstituted C_1-C_4 alkyl, said alkyl substituents being independently selected for the group consisting of hydroxyl, alkoxy, OR", CO_2H , CO_2R ", O_2CR " and combinations thereof; and

wherein Y is selected from the group consisting of hydrogen, R'', CO_2H , CO_2R'' , COR'', CN, $CONH_2$, CONHR'', $CONR''_2$, O_2CR'' , OR'' and halogen.

- 3. (Currently Amended) A method as claimed in claim $1 \frac{1}{1} \frac{1}{1$
- 4. (Currently Amended) A method as claimed in <u>claim 1</u> any preceding claim wherein the second source of radicals is a compound capable of forming a carbon or oxygen centred radical of Formula (8)

Wherein R2 and R3 are independently selected from the group R'; and W is a N=N bond, an O-O bond or a group that decomposes thermally or photolytically to form two residues containing a carbon or oxygen centred radical and at least one of R2 or R3 reacts with the polymer of Formula (6) or Formula (7) to leave the moiety R1 comprising the functional group.

- 5. (Original) A method according to claim 4, wherein R1, R2 and/or R3 may be the same or different and are selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups.
- 6. (Currently Amended) A method as claimed in claim 1 preceding claim wherein the group Z is selected from the group consisting of: methyl, ethyl, other C₁-C₄ alkyl, methylene covalently bonded to a polymer, methylene covalently bonded to a solid support T, phenyl, substituted phenyl, phenyl covalently bonded to a polymer, phenyl covalently bonded to solid support T, alkoxy, substituted alkoxy, thioalkoxy, substituted with a solid support T, benzyl, substituted benzyl, benzyl substituted with a polymer, benzyl substituted with a solid support T, SCH2.CH2.CO2T wherein T is a polymer or solid support and preferably SCH2.CH2.CO2T wherein T is a solid support or polymer.
- 7. (Original) A method as claimed in claim 6 wherein the group Z is selected from the group consisting of:

$$-S-R \longrightarrow CH_3$$

$$-C-H_2 \longrightarrow CH_3$$

$$-C-H_3 \longrightarrow CH_3$$

wherein T is a solid support selected from an organic compound, an inorganic compound or magnetised beads;

R is selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups;

n = an integer of at least 1

x = an integer greater than 1.

8. (Currently Amended) A method as claimed in <u>claim 1 wherein the</u> group R' and/or R1 any proceeding claim wherein the group R', R1, R2, R3 and/or R is selected from the group consisting of:

(Currently Amended) A method as claimed in claim preceding claim wherein the olefinically unsaturated monomer or of: comonomers are selected slected from the group consisting methyl methacrylate, ethyl acrylate, propyl methacrylate 2-ethylhexyl butyl methacrylate (all isomers), methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alphamethylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylates and acrylonitrile, styrene, styrenes selected glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), methacrylate, N, N-diethylaminoethyl N, N-dimethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, glycidyl acrylate, 2-hydroxyethyl acrylate, itaconic acid, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N, N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, И-N-tertmethylacrylamide, N, N-dimethylacrylamide, butylmethacrylamide, N-n-butylmethacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), pvinylbenzenesulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl tributoxysilylpropyl methacrylate, methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilypropylmethacrylate, dibutoxymethylsilylpropyl diisopropoxymethylsilylpropyl methacrylate, methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, methacrylate, diisopropoxysillpopyl dibutoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl diethoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl dibutoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl acrylate, vinyl fluoride, vinyl bromide, maleic anhydride, chloride, N-

phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene, propylene, 1,5-hexadienes, 1,4-hexadienes, 1,3-butadienes, and 1,4-pentadienes.

- 10. (Currently Amended) A method as claimed in claim 1 wherein the at least one olefinically unsaturated monomer is any of claims 1 to 8 wherein the polymerizable monomer or comonomers selected from the group consisting of: vinyl acetate, N-vinyl formamide, Nalkylvinylamine, allylamine, N-alkylallylamine, diallylamine, alkyldiallylamine, alkylenimine, acrylic acids, alkylacrylates, acrylamides, methacrylic acids, alkylmethacrylates, methacrylamides, N-alkylmethacrylamides, N-alkylacrylamides, styrene, vinylnaphthalene, vinyl pyridine, ethylvinylbenzene, aminostyrene, vinylanisole, vinylimidazolyl, vinylpyridinyl, vinylbiphenyl, dimethylaminomethylstyrene, trimethylammonium ethyl methacrylate, trimethylammonium ethyl acrylate, dimethylamino propylacrylamide, ethylacrylate, trimethylammonium trimethylammonium ethyl methacrylate, trimethylammonium propyl acrylamide, dodecyl acrylate, octadecyl acrylate, and octadecyl methacrylate.
- (Currently Amended) A method as claimed in claim 1 wherein the 11. at least one olefinically unsaturated monomer is a claimed in any of claims 1 to 8 wherein the polymerizable monomer or comonomers are group consisting of alkylacrylamides, selected from a methacrylamides, acrylamides, styrenes allylamines, allylammonium diallylamines, diallylammoniums, alkylmethacrylates, alkylacrylates, methacrylates, acrylates, n-vinyl formamide, vinyl ethers, vinyl acid, sulfobetaines, carboxybetaines, sulfonate, acrylic phosphobetaines, and maleic anhydride.

- 12. (Currently Amended) A method as claimed in claim 1 wherein at least one olefinically unsaturated monomer is claims 1 to 8 wherein the polymerizable monomer or comonomers are selected from the group consisting of: alkylmethacrylates, alkylacrylates, methacrylates, acrylates, alkylacrylamides, and styrenes.
- 13. (Currently Amended) A method as claimed in claim 1 wherein the first source of free radical any preceding claim wherein the first is selected from the group consisting of: initiator 2,2'azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid, 2-(tbutylazo)-2-cyanopropane, 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis (2-methylpropane), 2,2'-Azobis[2-(5-methyl-2-imidazolin-2,2'-Azobis[2-(2-imidazolin-2-2-yl)propane]dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2dihydrochloride, yl)propane] 2,2'-Azobis(2yl)propane disulfate dehydrate, methylpropionamide) dihydrochloride, 2,2'-Azobis [N-(2-carboxyethyl)-2,2'-Azobis[2-(3,4,5,6-2-methylpropionamidine]tetrahydrate, tetrahydropyrimidin- 2-yl)propane] dihydrochloride, 2,2'-Azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane], 2,2'-Azobis{2-methyl-N-[1,1bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-Azobis{2methyl-N-[2-(1-hydroxybuthyl)]propionamide}, 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile), 2,2'-Azobis(2,4-dimethyl valeronitrile), Dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-Azobis(2-methylbutyronitrile), 1,1'-Azobis(cyclohexane-1-carbonitrile), 2,2'-Azobis[N-(2-propenyl)-2-methylpropionamide], 1-[(cyano-1-methylethyl)azo] formamide, 2,2'-Azobis (N-butyl-2-methylpropionamide), 2,2'-Azobis (N-cyclohexyl-2methylpropionamide), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, di-

isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl, hyponitrite, and dicumyl hyponitrite.

(Currently Amended) Method according to claim 1, wherein the 14. second source of free radicals any preceding claim, wherein the second initiator is selected from the group consisting of : 2,2'azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid, butylazo) -2-cyanopropane, 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis (2-methylpropane), 2,2'-Azobis[2-(5-methyl-2-imidazolin-2,2'-Azobis[2-(2-imidazolin-2-2-yl)propane]dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2dihydrochloride, yl)propane] disulfate dehydrate, 2,2'-Azobis(2yl)propane methylpropionamide) dihydrochloride, 2,2'-Azobis[N-(2-carboxyethyl)-2,2'-Azobis[2-(3,4,5,6-2-methylpropionamidine]tetrahydrate, tetrahydropyrimidin- 2-yl)propane] dihydrochloride, 2,2'-Azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride, 2,2'-Azobis[2-(2-imidazolin-2-yl)propane], $2,2'-Azobis{2-methyl-N-[1,1-$ 2,2'-Azobis{2bis(hydroxymethyl)-2-hydroxyethyl] propionamide, methyl-N-[2-(1-hydroxybuthyl)]propionamide}, 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile), 2,2'-Azobis(2,4-dimethyl valeronitrile), Dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-Azobis(2-methylbutyronitrile), 1,1'-Azobis(cyclohexane-1-carbonitrile), 2,2'-Azobis[N-(2-propenyl)-2-methylpropionamide], 1-[(cyano-1-methylethyl)azo] formamide, 2,2'-Azobis (N-butyl-2-methylpropionamide), 2,2'-Azobis (N-cyclohexyl-2methylpropionamide), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, diisopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl, hyponitrite, and dicumyl hyponitrite.

- 15. (Currently Amended) A method as claimed in claim 1 any preceding claim when the reaction is carried out in a solvent selected from the group consisting of: water, alcohol, tetrahydrofuran dimethyl sulfoxide, dimethylformamide, acetone, acetonitrile, benzene, toluene and mixtures thereof.
- 16. (Currently Amended) A method as claimed in <u>claim 1</u> any preceding claim wherein a reaction is carried out at a temperature in the range of -20 to +200°C.
- 17. (Original) A method as claimed in claim 16 wherein the reaction is carried out at a temperature in the range of 20 to 150° C.
- 18. (Original) A method as claimed in claim 17 wherein the reaction is carried out at a temperature in the range of 20 to 120°C.
- 19. (Original) A method as claimed in claim 18 wherein the reaction is carried out at a temperature in the range of 60 to 90° C.
- 20. (Currently Amended) A method according to <u>claim 1</u> any preceding claim comprising the step of reacting a first supported thiocarbonyl thio compound of Formula (3) or Formula (4) with the olefinically unsaturated monomer (Q) and the first source of free radical to form a polymer of Formula (6) or Formula (7) in the presence of a second non-supported thiocarbonyl compound, and the first and second thiocarbonyl having identical groups R'.
- 21. (Original) A method of carrying out a reversible-addition-fragmentation chain transfer (RAFT) polymerisation comprising the

steps of reacting olefinically unsaturated monomers with a first supported chain transfer agent, in the presence of a second unsupported chain transfer agent, in the presence of a free radical source, to form a polymer.

- 22. (Currently Amended) A method according to claim 20 or claim 21 comprising a greater concentration of supported compound than non-supported compound.
- 23. (Currently Amended) A method of producing a block copolymer comprising reacting a first unsaturated monomer by a method according to claim 1 any one of claims 1 to 20, wherein the thiocarbonyl thio compound of Formula (3) is supported on a solid support, recovering polymer attached to the solid support, and then reacting the recovered polymer by the method of claim 1 any one of claims 1 to 20 with a second unsaturated monomer to form a block copolymer.
- 24. (Currently Amended) A compound for use in a method according to claim 1 any preceding claim comprising the formula:

$$z = \begin{bmatrix} S \\ -S - R^{\mathsf{y}} \end{bmatrix}_{\mathsf{m}}$$

Formula (3)

$$\left[z - \frac{S}{J_p}R^{1}\right]$$

Formula (4)

where:

Z is a solid support or a solid support attached via a linker to the thiocarbonyl thio moiety,

m = an integer of at least 1,

p = an integer of at least 1,

R' is selected from the group consisting of alkyl, substituted substituted alkoxy, aromatic saturated alkoxy, an unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups.

25. (Original) A polymer having the formula:

$$z = \begin{bmatrix} S & & & \\ & & & \\ & & & \\ & & & \end{bmatrix}_{q} = R^{1}$$
(6)

$$\left[z - S - Q \right]_{q_{p}} R^{y}$$
(7)

where:

Z is a solid support or a solid support attached via a linker to the thiocarboxyl thio moiety,

m = an integer of at least 1,

p = an integer of at least 1,

q = an integer of at least 2,

is selected from the group consisting of alkyl, substituted alkoxy, substituted alkoxy, an aromatic saturated unsaturated carbocyclic or heterocyclic ring, optionally substituted cyanoalkyl, with one or more substituents, amino alkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups,

Q is at least one olefinically unsaturated monomer, optionally two or more different olefinically unsaturated monomers.

26. (Currently Amended) A compound or polymer according to claim 24 or claim 25,

wherein Z is selected from:

wherein T is a solid support selected from an organic compound, an inorganic compound or magnetised beads,

R is selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups,

n = an integer of at least 1.

- 27. (Currently Amended) A polymer obtainable by a method according to claim 1 any one of claims 1 to 22.
- 28. (New) A method as claimed in claim 4 wherein the group R2 and/or R3 is selected from the group consisting of:

29. (New) A method as claimed in claim 6 wherein the group R is selected from the group consisting of:

30. (New) A compound or polymer according to claim 25, wherein Z is selected from:

wherein T is a solid support selected from an organic compound, an inorganic compound or magnetised beads,

R is selected from a group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups,

n = an integer of at least 1.